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ELECTROCHEMISTRY OF INTERHALOGEN CATHODES (U)

FINAL REPORT

(21 April 1969 to 21 March 1970)

May 1970

By

M. M. Nicholson

Prepared Under Contract N00019-69-C-0456

For

Naval Air Systems Command
Department of the Navy

By

Atomics International

A Division of North American Rockwell Corporation
P. O. Box 309, Canoga Park, California 91304

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ABSTRACT

Halogen fluoride cathodes offer the prospect of extremely high energy densities when combined with active metal anodes in electrochemical power sources. Chlorine trifluoride, with a theoretical 2120 whr/lb in combination with lithium, is also known to support substantial current densities when dissolved in anhydrous hydrogen fluoride containing an alkali metal fluoride electrolyte. The objective of this program was the further evaluation of chlorine trifluoride as a power source cathode material. A half-cell study was made on dilute ClF_3 solutions at 5°C in 1 M NaF-HF by the cyclic voltammetric technique, using platinum electrodes. Three cathodic and two anodic reactions were observed in wide-span voltammograms on this system. One of the electrode processes showed a high degree of reversibility, which suggests its use in a secondary, as well as a primary, cell. The potential of this couple corresponds to 4.8 v with respect to a lithium anode. Reverse reactions did not occur with the other processes. Further investigation will be required to identify the products of the various electrode reactions, and thus to establish, with certainty, the energy densities that might be expected in optimized chlorine trifluoride cells.

Pure lithium is chemically incompatible with hydrogen fluoride. A dual-solvent cell containing a liquid lithium anode dissolved in liquid ammonia and an interhalogen cathode in hydrogen fluoride is under consideration by the Navy. Some technical problems involved in the construction of such a cell are discussed in this report, and the possibility of using a solid electrolyte separator is suggested. Lithium alloy anodes that would function directly in HF are also considered for an alternative single-solvent cell.

Recommendations for further work on the ClF_3 cathode include the identification of electrode reactions, optimization studies using less expensive substrates than platinum, and the investigation of temperature dependence.

I. INTRODUCTION

A lithium-fluorine cell offers the highest theoretical energy density that might be attained from an electrochemical power source composed of stable materials. The thermodynamic value of 2830 whr/lb for this cell is more than ten times the corresponding energy density for the silver-zinc battery. For practical reasons, principally relating to materials compatibility, other systems such as lithium-cupric fluoride (744 whr/lb) have received more emphasis in recent programs for the development of batteries to be used in a moderate temperature range. These less energetic systems have presented other problems, however, including slow cathode reactions and poor conductivity of electrolytes in the organic solvents that are compatible with lithium. In this program, attention was turned again to cathode materials with reactivities approaching that of elemental fluorine and to inorganic electrolytes.

It was known from earlier investigations that chlorine trifluoride is cathodically active when dissolved in anhydrous hydrogen fluoride⁽¹⁾ or in bromine trifluoride.⁽²⁾ The ClF_3 -NaF-HF system was selected for further evaluation in this program. Characterization of the electrode process was a major objective, since the performance of the system as a power source cathode will depend on the stoichiometry and kinetics of the various reactions that may occur. Initial studies for this purpose were made with platinum electrodes in dilute ClF_3 solutions by the cyclic voltammetric technique. Subsequent work is expected to include a similar investigation with other substrates, as well as cathodic discharge measurements at higher current densities and reactant concentrations.

This study on the Electrochemistry of Interhalogen Cathodes was performed by Atomics International, one of the Power Systems Divisions of North American Rockwell Corporation. It was undertaken as one of the principal tasks in a three-part Navy program to develop an ultrahigh-energy battery for use at ambient or lower temperatures. It is visualized that an interhalogen cathode may be combined with a liquid lithium ammoniate anode⁽³⁾ if a suitable separator⁽⁴⁾ can be found for such a dual-solvent cell. Other anodes, including lithium alloys, which might be usable directly in hydrogen fluoride, offer the possibility of a much simpler separator structure without too great a sacrifice of energy density.

II. EXPERIMENTAL

Special equipment that was designed and constructed for handling ClF_3 and HF before and during the electrochemical measurements is described in Section II-A-1. Section II-A-2 describes the electrochemical cell and electrodes in detail. Experimental procedures are given in Section II-B.

A. APPARATUS

1. ClF_3 -HF System

The schematic design of the system for handling chlorine trifluoride and hydrogen fluoride is shown in Figure 1. The basic operations performed with this equipment were (1) purification of the two low-boiling materials, (2) collection and transfer of known quantities into the electrochemical cell, and (3) disposal after completion of the experimental measurements. Nitrogen was used to purge the system before and after an

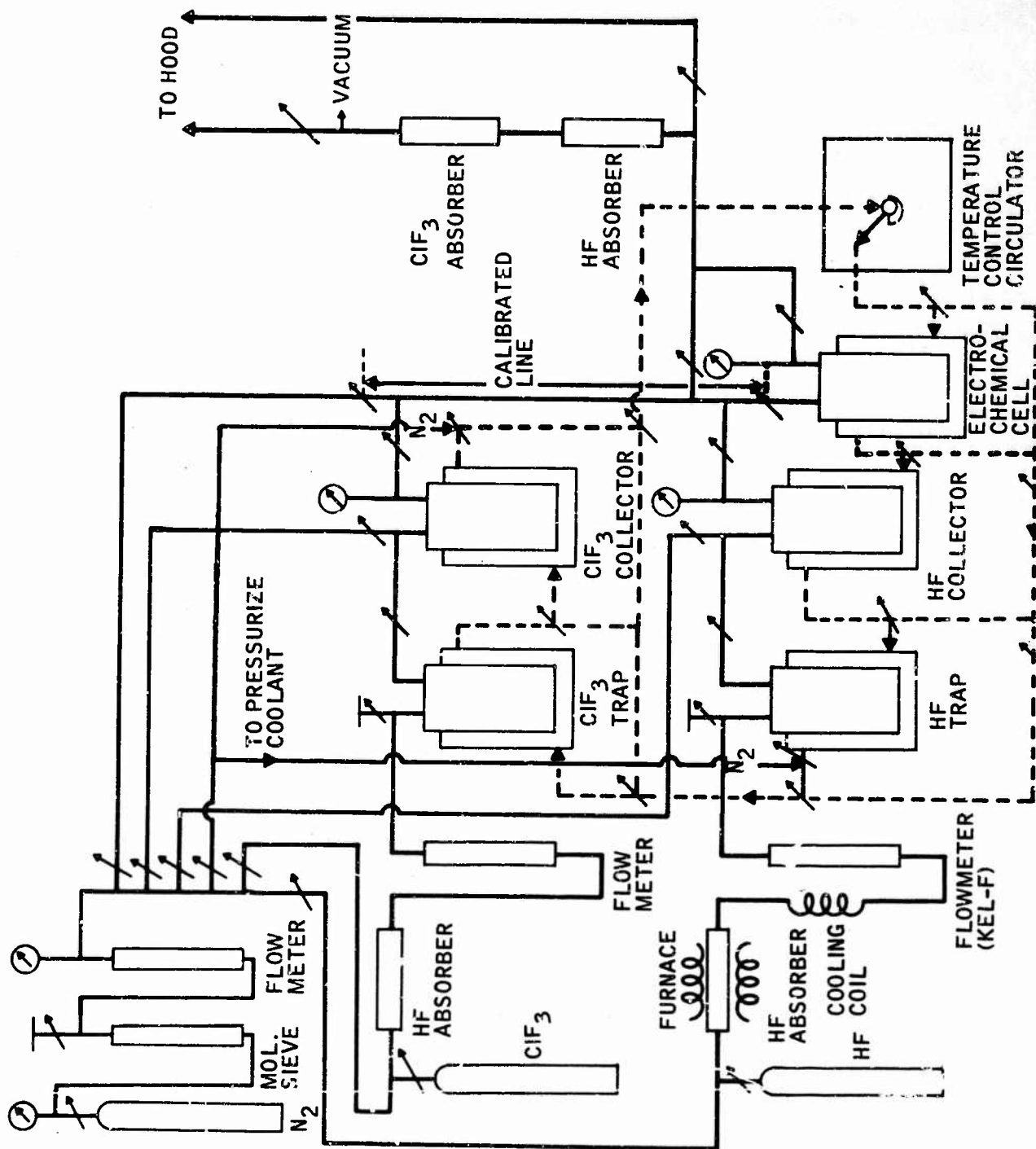
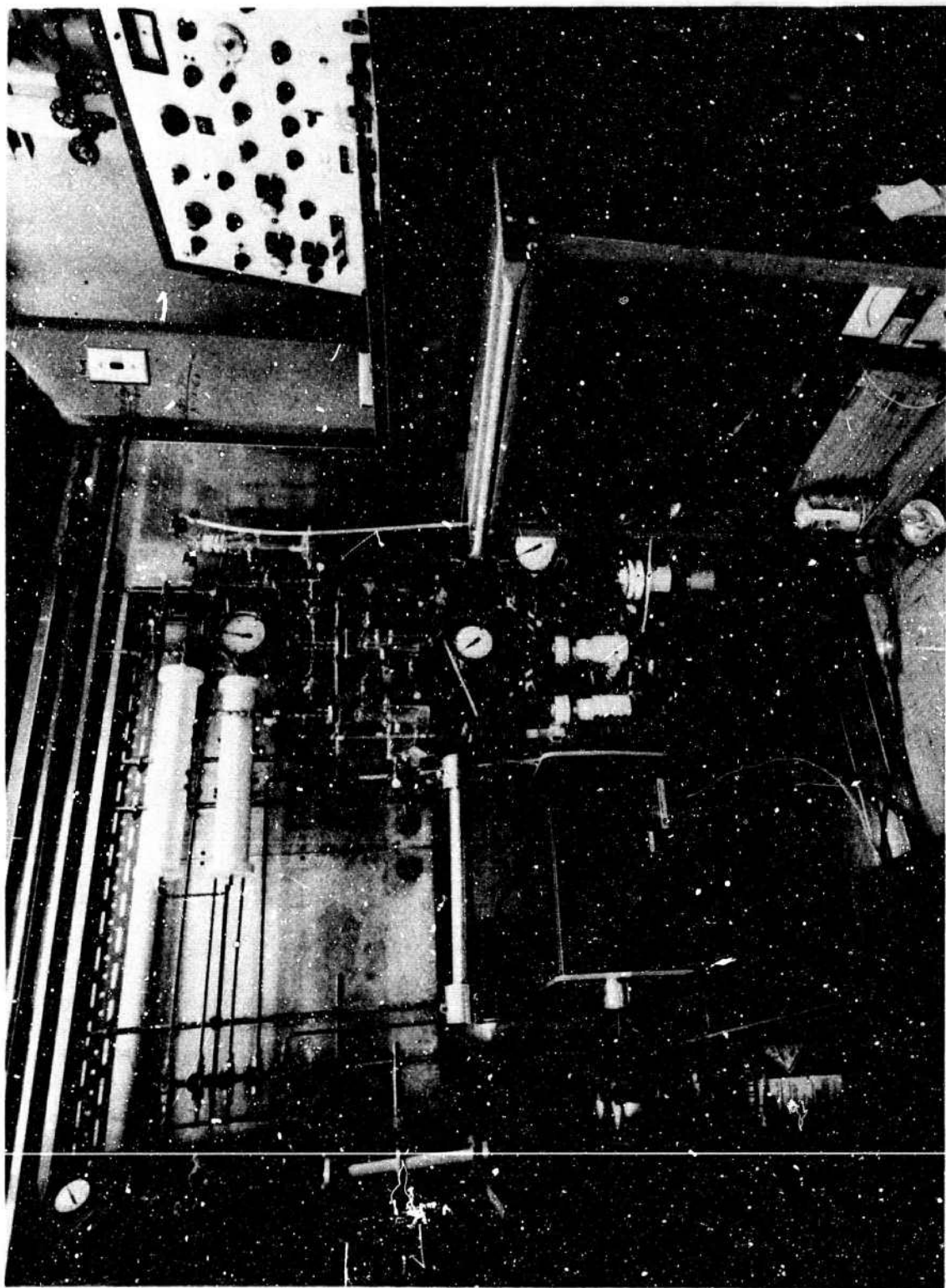


Figure 1. Schematic Design of ClF_3 -HF System

experiment and to facilitate the transfer of materials by distillation or gas displacement. Figure 2 is a general photographic view of the entire apparatus assembled in the walk-in hood. Component part numbers and construction details are given in the next paragraphs.

Miscellaneous Components. Parts of the system exposed to corrosive environments were assembled from 1/4-in. Monel tubing, Monel valves (Hoke 2235F2M and 3232M4M), and Monel Gyrolok fittings. For easier detachment, some of the Monel ferrules inside the fittings were replaced with Teflon. The N_2 , ClF_3 , and HF lines were equipped with pressure relief valves set for 30, 50, and 50 psig, respectively. The pressure gages were Crosby Ashton Style AMO-304A4, zero-center, with Monel Bourdon tubes and sockets. All parts were carefully cleaned and degreased with trichloroethane before final assembly. Threaded fittings were then sparingly lubricated with Hooker GR-290 Kel-F grease, or sealed, in some cases, with virgin Teflon tape.

ClF_3 System. Chlorine trifluoride from the supply cylinder was passed through an absorber column containing sodium fluoride pellets to remove hydrogen fluoride before it entered the glass metering and collection system. The NaF was prepared by thermal decomposition of technical grade $NaHF_2$ pellets from Baker and Adamson. The absorber column was constructed of 2-in.-diameter Inconel pipe, flanged at each end, and sealed with a gasket of high-purity aluminum. The ClF_3 trap, which was designed to accommodate any splashing of liquid samples, was fabricated from conical-end Pyrex pipe, with a Monel cap and Teflon O-ring seal. The ClF_3 collector, for the storage of liquid or gaseous ClF_3 , was of the same design.



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Figure 2. General View of Apparatus

HF System. A sodium fluoride column in the HF line was used in the removal of water from hydrogen fluoride, as described in Section II-8-2.⁽⁵⁾ For this purpose, the column was placed in a Lindberg Hevi-Duty Model 54231-A tube furnace. The column was constructed of Inconel, aluminum-sealed, with essentially the same design as that in the ClF_3 system. The HF flow was monitored on a Brooks-Mite Model 2101, Size 6, Kel-F flowmeter. A coil of 1/4-in. diameter Monel tubing, with an extended length of 180 cm, was inserted immediately after the main HF absorber to prevent overheating of the flowmeter during the HF regeneration process. Air circulation within the hood provided adequate cooling for this coil. The HF trap and collector were machined from 3-in.-diameter Teflon rod, with Teflon covers and Teflon O-ring seals. Outer retaining rings were of Monel and aluminum.

Disposal Units. The disposal columns for HF and ClF_3 contained sodium fluoride pellets and soda lime, respectively. These units were made from 3-in.-diameter Teflon pipe, with Teflon screw caps and O-ring seals.

Temperature Control. Each of the liquid containers and traps was equipped with a Pyrex jacket for temperature control. The jackets were attached to the containers and their lower retaining rings through rubber O-rings, which formed three-way liquid-tight seals. The coolant was a fluorocarbon liquid, FC-77, from Minnesota Mining and Manufacturing Co. A network of Teflon tubing and valves connected the temperature-control jackets into a continuous system, as indicated in Figure 1. With this arrangement, the liquid could be circulated through any one of the cooling

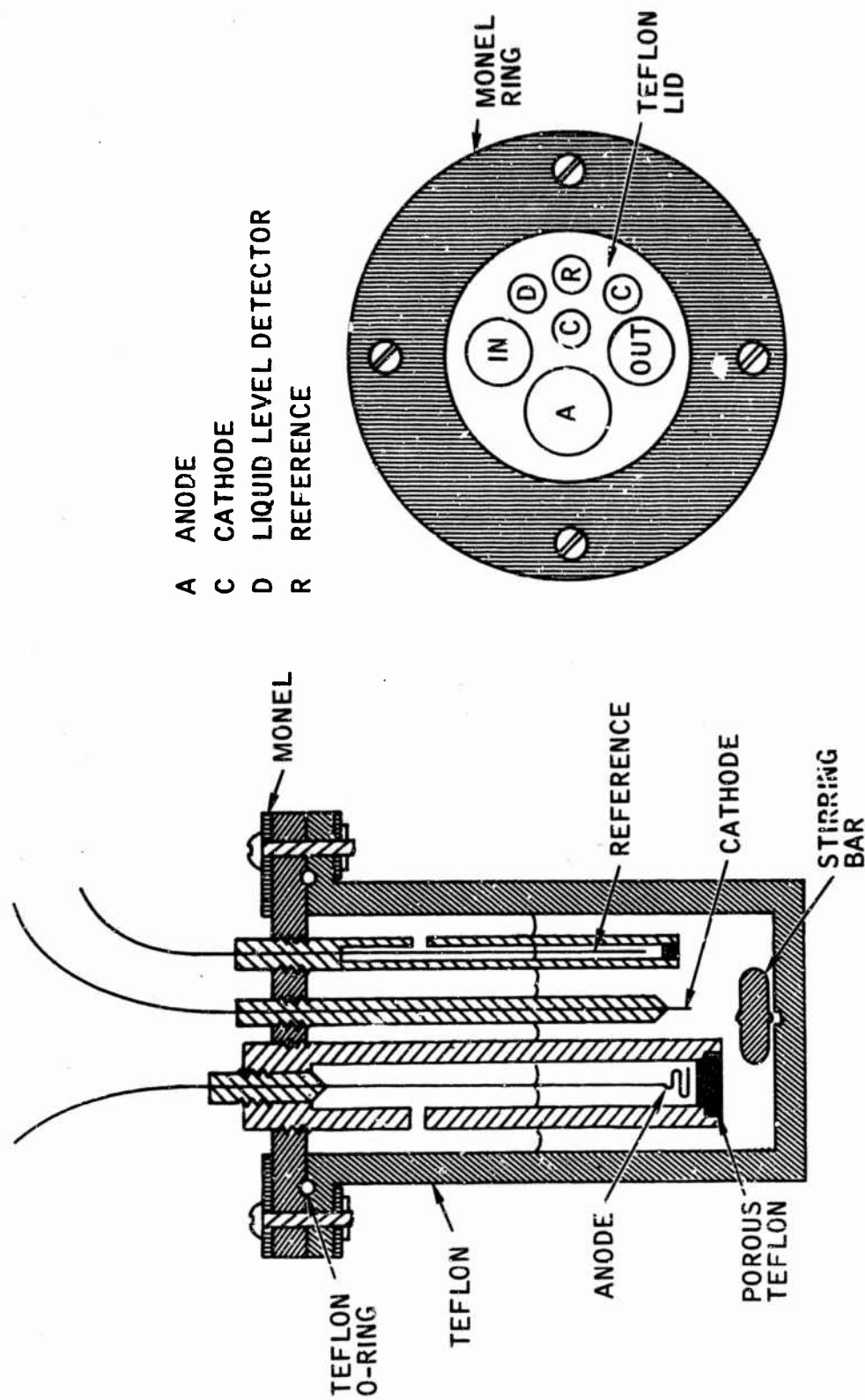
jackets, or through several of them in series. The circulation unit was a Haake Type N-64 circulator bath, with the control heater modified to operate on a variable transformer. A 1/8-hp Tecumseh Model P91L refrigeration unit, connected to an enlarged heat transfer coil in the bath, provided the primary cooling. This automatic equipment produced a minimum cell temperature of approximately 4°C, as measured by a Chromel-Alumel thermocouple junction located in the coolant line preceding the cell jacket.

2. Cell and Electrodes

The electrochemical cell design is shown schematically in Figure 3. The cell body and interior components were of Teflon, including sections of the inlet and outlet tubes that extended below the lid. The anode and reference electrode compartments were separated from the cathode section by porous Teflon disks. Two cathodes could be mounted simultaneously in the cell. A shorter electrode of similar structure served as a liquid level detector. Figure 4 shows the detailed construction of the electrode holders, which were designed with threaded connections to provide pressure seals at all metal-Teflon and Teflon-Teflon surfaces. Figure 5 is a photograph of the cell and its temperature-control jacket. The scale is shown in inches.

The cell contained five wire electrodes, of the compositions and sizes indicated below.

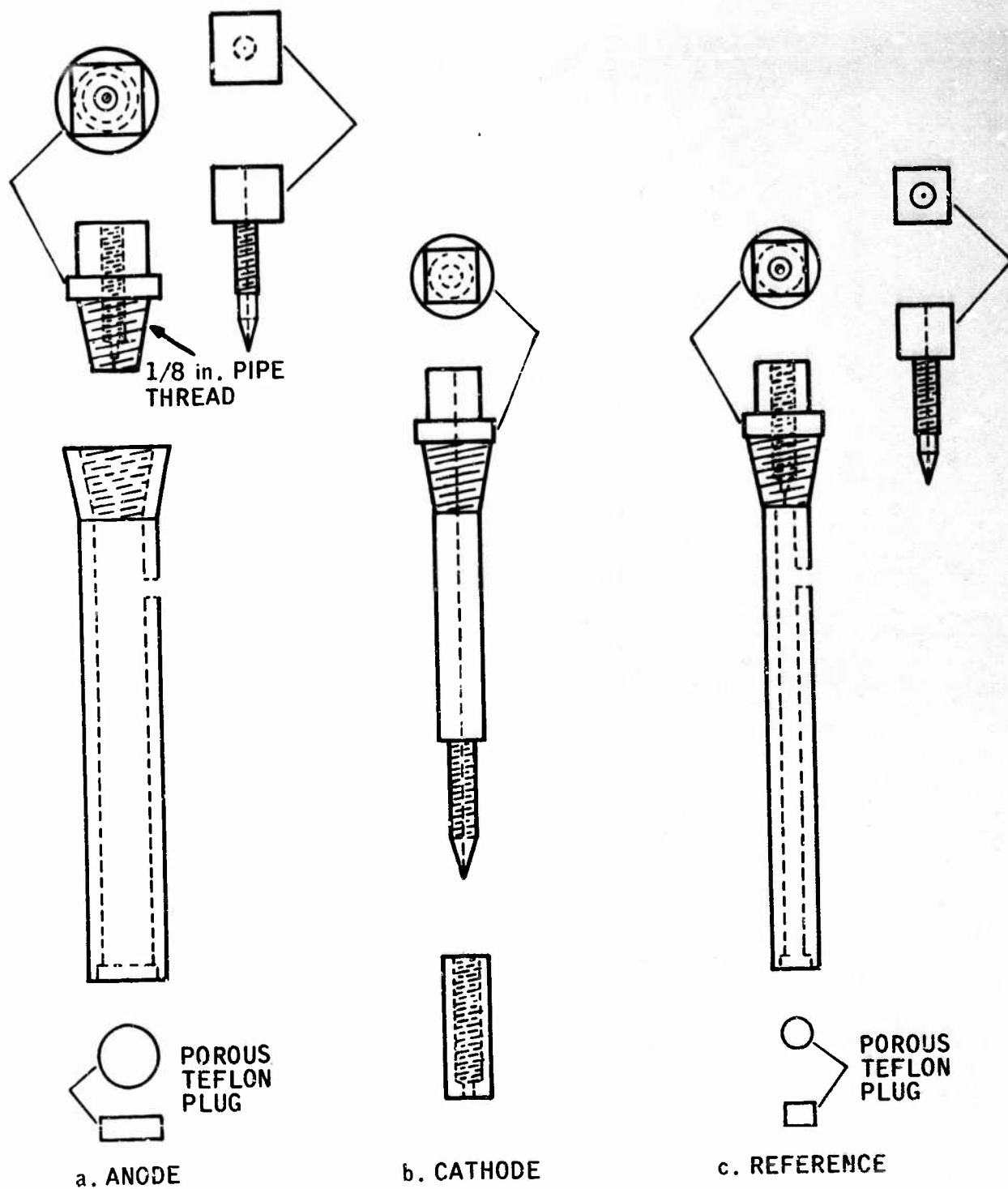
<u>Electrode</u>	<u>Composition</u>	<u>Diameter (cm)</u>	<u>Area₂ (cm)²</u>
Cathode No. 1	Pt	0.0508	0.160
Cathode No. 2	Pt	0.0508	0.160
Anode	Cu	0.081	5.6
Reference	Cu/CuF ₂	0.0488	0.16
Liquid Level Detector	Cu	0.0287	~0.01



a. SIDE VIEW, SHOWING ANODE, REFERENCE ELECTRODE, AND ONE CATHODE

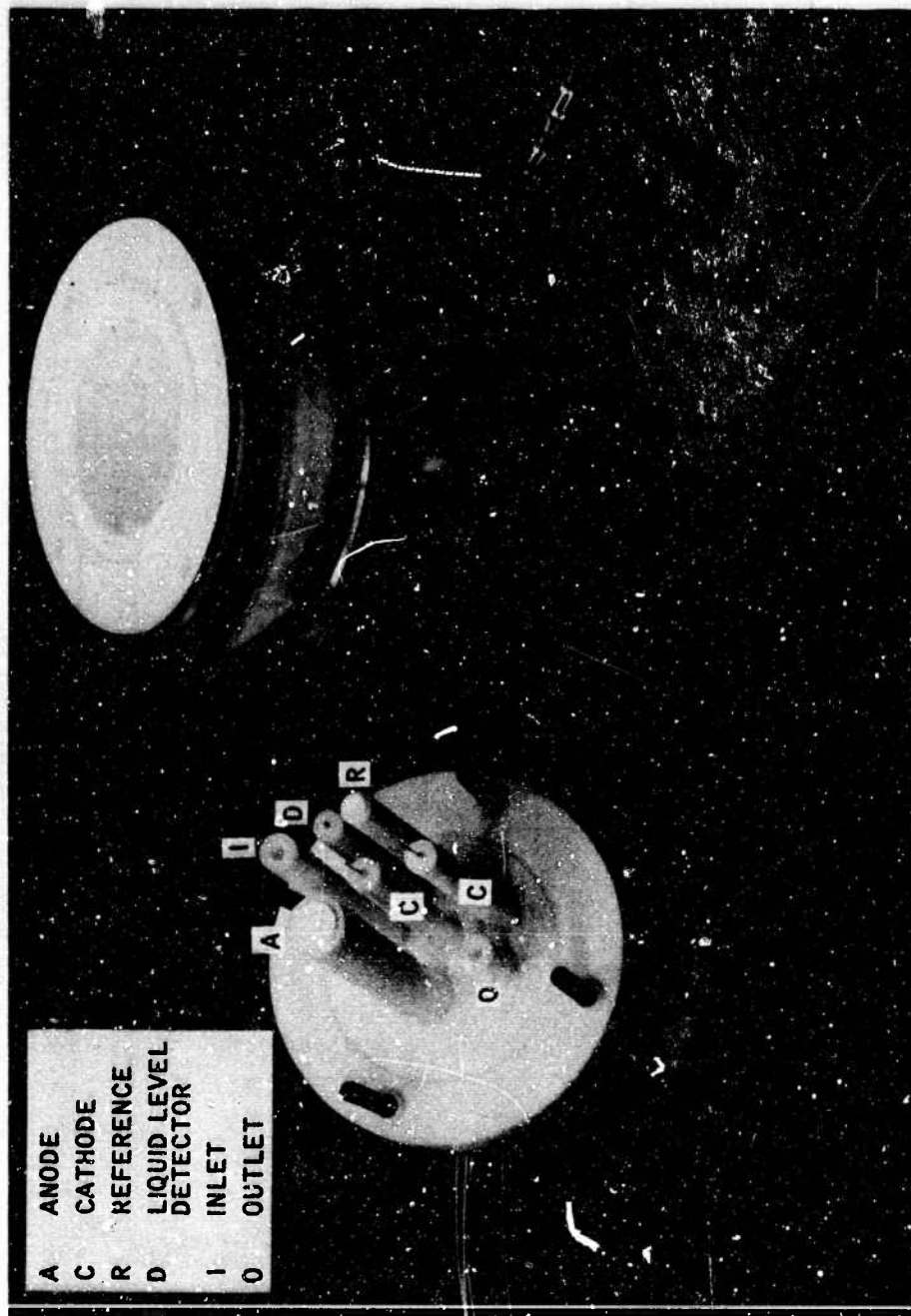
b. TOP VIEW, SHOWING POSITIONS OF INSERTS

Figure 3. Schematic Design of Electrochemical Cell



W. F. GOEPPINGER

Figure 4. Teflon Electrode Holders



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Figure 5. Electrochemical Cell

B. PROCEDURES

This section describes procedures for the passivation of metal equipment, in situ preparation of the solutions and reference electrode, and acquisition of the electrochemical data.

1. Passivation of Metal Surfaces

Interior metal surfaces in the HF-ClF₃ system, with the exception of the electrodes, were passivated by successive exposures to 0.3 and 0.5 atm of ClF₃, diluted with nitrogen to a total pressure of 1 atm. A pressure drop of 0.1 atm indicated that most of the ClF₃ uptake occurred in the first 5 minutes. Some of this drop may have been due to adsorption of ClF₃ on NaF in the absorber columns. The equipment was then allowed to stand overnight in contact with gaseous ClF₃ to assure the complete formation of protective films.

2. Preparation of Solutions

Hydrogen fluoride for the electrochemical work was prepared by thermal decomposition of previously-dried sodium bifluoride, essentially as described by Runner, Balog, and Kilpatrick.⁽⁵⁾ The regeneration of HF from NaHF₂ pellets proceeded smoothly at 395°C or above, without damage to the pellet structure. Difficulty was encountered from the formation of a molten salt phase, however, upon reabsorption of HF into NaF at the recommended temperature of 200°C; an improved absorption procedure will be developed as the program continues. The primary HF supply was a cylinder of 99.9% material from the Matheson Company.

The dried HF was condensed directly into the electrochemical cell, which contained a weighed quantity of NaF powder, sufficient to make 50 ml of a 1 M solution. The sodium fluoride for the electrolyte was Baker's

Analyzed Reagent, 99.6% pure,* which was further dried at 200°C. Dissolution was assisted by a magnetic stirrer, as the hydrogen fluoride condensed in the cell. Attainment of the 50 ml liquid level was observed by monitoring the open-circuit potential of the small level detector electrode against the copper anode. This potential stabilized abruptly when the detector came into contact with the liquid. At that time, the collection of HF was stopped.

Chlorine trifluoride was added to the closed electrochemical cell from a calibrated 17.3-ml section of Monel tubing, in which the gas had been trapped at the prevailing room temperature and a pressure of 1 atm. Transfer into the cell was accomplished by means of nitrogen, pressurized at 2 to 7 psig. The solution was stirred during this operation. Rapid dissolution of ClF_3 was indicated by an immediate rise of several tenths of a volt in the platinum electrode potential. The solution resulting from a single addition of the gas was 0.014 M in ClF_3 .

3. Preparation of Reference Electrode

The Cu/CuF_2 reference electrode was prepared by anodizing a Grade 5N copper wire for several minutes at 0.5 mA/cm^2 in the NaF-HF electrolyte solution before the addition of ClF_3 .⁽⁵⁾

4. Electrochemical Measurements

The electrochemical data consisted of open-circuit potentials and single-sweep and cyclic voltammograms with linear variation of the applied potential. These measurements were made with a Princeton Applied Research Model 170 Electrochemistry System. Data were recorded at several sweep rates ranging from 20 to 500 mV/sec .

*Principal impurities were: loss on drying, 0.08%; free alkali as (Na_2CO_3) , 0.10%; insoluble matter, 0.01%.

III. DISCUSSION

Before the discussion of results obtained on the ClF_3 cathode, some background information on halogen and interhalogen cells is considered in Section III-A. The experimental results are then presented in Section III-B.

A. LITHIUM-INTERHALOGEN CELLS

1. Cathodes

Table 1 gives theoretical characteristics of lithium cells with elementary fluorine and chlorine, and with several halogen fluorides, as cathode materials. Chlorine pentafluoride⁽⁹⁾ was excluded from this initial list because of possible handling difficulties. The excessive vapor pressure of fluorine (b.p. -188°C) limits its usefulness in self-contained battery systems. The energy density of the $\text{Li}-\text{ClF}_3$ combination is only 25% lower than that of $\text{Li}-\text{F}_2$, if complete reduction to fluoride and chloride ions occurs, and the vapor pressure of ClF_3 is a moderate 1.7 atm at 25°C . It should be noted that other products could be produced by less complete cathodic reduction of ClF_3 . Energy densities for the intermediate reduction stages, yielding ClF and Cl_2 , are also given in Table 1. Although these values are lower than the optimum of 2120 whr/lb, they are still much higher than that of any conventional cell.

Chlorine trifluoride is miscible in all proportions with anhydrous HF. At 25°C , the maximum vapor pressure of this binary system is 1.8 atm; the azeotrope then contains 67 mole % ClF_3 .⁽¹²⁾ Thermodynamically, ClF_3 is the first choice among the cathode materials included in Table 1, when both vapor pressures and free energies are considered. Additional vapor pressure and freezing point data for the ClF_3 -HF system and the NaF -HF electrolyte are given in Tables 2 and 3.

TABLE 1
THERMODYNAMIC CHARACTERISTICS OF LITHIUM-HALOGEN AND
LITHIUM-INTERHALOGEN CELLS AT 25°C

Material	Cathode		Assumed Cell Reaction	E° Cell (volts) ^c	Energy Density (whr/lb) ^d
	Boiling Point (°C) ^a	ΔF_f° (kcal/mole) ^b			
F ₂	-188	0	2Li + F ₂ → 2LiF	6.05	2830
Cl ₂	-34.1	0	2Li + Cl ₂ → 2LiCl	3.98	1140
ClF	-100.8	-13.6 ⁽⁷⁾	2Li + ClF → LiF + LiCl	4.72	1680
ClF ₃	11.8	-27.2 ⁽⁷⁾	4Li + ClF ₃ → 3LiF + LiCl	5.24	2120
			3Li + ClF ₃ → $\frac{1}{2}$ Cl ₂ + 3LiF	5.66	1820
			2Li + ClF ₃ → ClF + 2LiF	5.76	1380
BrF	-	-18.0 ⁽⁸⁾	2Li + BrF → LiF + LiBr	4.40	948
BrF ₃	135	-55.2 ⁽⁸⁾	4Li + BrF ₃ → 3LiF + LiBr	4.82	1420
BrF ₅	40.5	-84.1 ⁽⁸⁾	6Li + BrF ₅ → 5LiF + LiBr	5.02	1690

^aAt 1 atmosphere

^bStandard free energy of formation of the gaseous cathode material at 25°C

^cFor gaseous cathode materials; solid anodes and reaction products

^dBased on weights of active electrode materials

TABLE 2

VAPOR PRESSURES IN THE ClF_3 -HF SYSTEM

Temperature (°C)	Vapor Pressure (mm Hg)		
	ClF_3 ⁽¹⁰⁾	HF ⁽¹¹⁾	ClF_3 -HF Azeotrope ⁽¹²⁾
-10	277	235	640
0	451	352	
10	705	531	
11.8	760		
19.4		760	1150*
20	1065	770	

*66.5 mole % ClF_3

TABLE 3

FREEZING POINTS IN THE ClF_3 -HF-NaF SYSTEM

Material	Freezing Point (°C)
ClF_3	-76.3
NaF in HF ⁽¹³⁾ (mole fr HF)	
1.00	-92.3
0.98 (1 M NaF)	-
0.91	-40
0.88	0
0.85	25
0.80	39.8

Previous investigators have observed that chlorine trifluoride is also promising kinetically, although the reduction products were not identified.^(1,2) The cathodic behavior of ClF_3 has been examined in relation to power source applications in liquid HF solutions at 3°C , in molten $\text{KF}\cdot\text{HF}$ at 85°C , and in BrF_3 at several temperatures. A current density of 20 ma/cm^2 on a porous carbon electrode was reported for the reduction of ClF_3 in liquid HF, and 5 ma/cm^2 , in the $\text{KF}\cdot\text{HF}$ electrolyte.⁽¹⁾ Current densities of the order of 1 ma/cm^2 without severe polarization were observed for ClF_3 on a smooth platinum cathode in a BrF_3 solvent; addition of BF_3 to the liquid system increased the conductivity and may have had other beneficial effects on the overall performance of the cell, which included a cadmium anode.⁽²⁾ Pure BrF_3 and $\text{BrF}_3\text{-BF}_3$ mixtures also showed enough cathodic activity to support currents of several ma/cm^2 .⁽²⁾

With this background of established feasibility, the ClF_3 cathode in a NaF-HF electrolyte was selected for further investigation in the present program. Some conductivities in this system are given in Table 4.

TABLE 4
CONDUCTIVITIES IN THE $\text{ClF}_3\text{-HF-NaF}$ SYSTEM

Material	Temperature ($^\circ\text{C}$)	Specific Conductance ($\text{ohm}^{-1}\text{cm}^{-1}$)
ClF_3 ⁽¹⁴⁾	-78 25	6.5×10^{-9} 4.9×10^{-9}
HF ⁽⁵⁾	0	3×10^{-6}
0.5 M NaF in HF ⁽¹⁵⁾	0	6.5×10^{-2}
1 M*	0	$\sim 6 \times 10^{-2}$

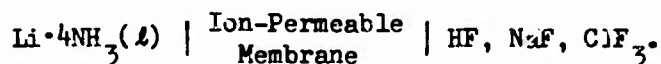
*Estimated by extrapolation of Λ/Λ_0 vs \sqrt{m}

2. Anodes

Because of its high chemical reactivity, pure lithium cannot be used directly as an anode in anhydrous hydrogen fluoride or in a reactive aprotic solvent such as bromine trifluoride. Two approaches for stabilization of the anode system are described briefly in this section.

a. Lithium Dissolved in Liquid Ammonia

A two-electrolyte system with the anode and cathode in different solvents offers a challenging possibility for construction of a $\text{Li}-\text{ClF}_3$ cell, provided the exacting separator requirements can be met. The Navy's interest in the dual system was stimulated by the observation that lithium ammoniate has sufficient chemical stability for use as a liquid anode material.⁽³⁾ The high electronic conductivity of the lithium bronze phase, with the approximate composition $\text{Li} \cdot 4\text{NH}_3$, is another advantageous feature. A complete cell would then be represented by



Inert current collectors, not shown here, would be provided for both liquid electrode systems.

b. Lithium Alloys

A lithium alloy anode would greatly simplify the separator problem. Some information supporting the feasibility of the alloy electrode is available from previous investigations. Lithium-magnesium alloy anodes have been patented for use in aqueous medium.⁽¹⁶⁾ The open-circuit potential of an alloy containing 35 % Li was 0.6 v more positive (less active) than that of pure lithium, and the corrosion rate was not excessive. At a current density of 125 ma/cm^2 , the potential of this alloy

was slightly better than that of pure magnesium. The lithium-magnesium alloy LA-141* has been investigated as an anode in a molten LiCl-KCl electrolyte.⁽¹⁷⁾ Magnesium was preferred in that case because of its higher melting point, but the alloy was active electrochemically, with the consumption of both lithium and magnesium. Solid lithium-aluminum alloys are also effective battery anodes in molten LiCl-KCl.⁽¹⁸⁾

To use a lithium alloy anode in HF, one must achieve a balance between passivity, which prevents excessive corrosion, and anodic activity under external current drain. This compromise can be approached by changing the alloy composition. Both magnesium and aluminum tend to passivate in fluoride media and even in ClF_3 .⁽¹⁹⁾ Thus, the alloy anode in HF does not seem an impractical goal. A pure magnesium or pure aluminum anode also can be considered, but control of passivity may be more difficult in those cases.

Theoretical potentials and energy densities of ClF_3 cells with several different anodes are given in Table 5, and the corresponding separator requirements are noted. The tabulated data are based on the free energies of materials in the indicated standard states, with the exception of the Li-Mg alloy, for which the open-circuit potential in aqueous solution was used.⁽¹⁶⁾ Solvation energies were not taken into account in preparing this table.

3. Separators

The passivated alloy anodes do not impose exceptional requirements on the separator. Self-discharge would be reduced by interposing a barrier of fine-porosity Teflon or other inert material between

*13-15% Li, 1.0-1.5% Al, 84-86% Mg, plus minor components

TABLE 5
CHARACTERISTICS OF ClF_3 CELLS WITH SEVERAL ANODE MATERIALS AT 25°C

Anode	Assumed Cell Reaction	Thermodynamic ^a		Desired Solvent	Separator Requirement
		E°_{Cell} (volts)	Energy Density (whr/lb)		
Li	$4\text{Li} + \text{ClF}_3 \rightarrow \text{LiCl} + 3\text{LiF}$	5.24	2120	NH_3 for anode; HF for cathode	Diffusion and intersolvent barrier
Li-Mg Alloy	$4\text{LiMg}_{0.53} + \text{ClF}_3 \rightarrow \text{LiCl} + 3\text{LiF} + 2.12 \text{ Mg}$	4.64 ^b	1310 ^c	HF	Diffusion barrier
Mg	$4\text{Mg} + 2\text{ClF}_3 \rightarrow \text{MgCl}_2 + 3\text{MgF}_2$	4.55	1570	HF	Diffusion barrier
Al	$4\text{Al} + 3\text{ClF}_3 \rightarrow \text{AlCl}_3 + 3\text{AlF}_3$	3.44	1304	HF	Diffusion barrier

^aFor gaseous cathode material, solid anodes and reaction products

^b E°_{Cell} based on aqueous solution data for alloy (16)

^cWeight of magnesium included but only lithium consumed anodically

the solid alloy anode and the cathode region containing dissolved chlorine trifluoride. Nonporous separators with sufficient ionic conductivity would also be appropriate.

The dual-solvent cell presents several problems. With two liquid electrode systems, the danger of self-discharge through direct chemical interaction of the electrode materials is more severe. Furthermore, the incompatible solvents, NH_3 and HF , must not be permitted to mix. The separator should therefore be permeable only to ions and should be inert to both dissolved lithium and chlorine trifluoride. Three classes of materials might be considered for this purpose:

a. Organic Ion Exchange Resins

Polymeric ion exchange resins, including perfluorinated types, have been investigated by the General Electric Company in a related Navy program.⁽⁴⁾ Although it was recognized that this type of membrane alone cannot meet all of the separator requirements in a dual solvent NH_3 - HF cell, it was found that certain membranes would function in the individual solvents. They could be useful, therefore, as elements in multicomponent separators.

b. Inorganic Fluoride-Specific Membranes

Lanthanum fluoride crystals doped with europium have very high specificity for the transport of fluoride ion.^(20,21) This characteristic has led to their use in fluoride-specific electrodes which are analogous to the glass electrode for hydrogen ion. The membrane resistance is not critical in this potentiometric application; a value of 2×10^5 ohms is typical of a commercial fluoride-specific electrode.⁽²¹⁾ Such membranes

have been used also in the coulometric generation of fluoride ion.⁽²²⁾ In that case, the resistance of a plate 9 mm in diameter and 1.5 mm thick was 1.3×10^4 ohms. Although this resistance is too high for a battery separator that must operate under moderate or high current densities, it is possible that lanthanum fluoride membranes may find applications for interim experimental purposes and that more conductive solids in this general class might eventually be developed. The Orion fluoride electrode is stable in 25% HF and in 50% NaOH, which suggests dual-solvent capability. No data for the solubility of lanthanum fluoride in liquid ammonia have been found. If this solubility is low enough, an additional inert porous separator might then be adequate to protect a lanthanum fluoride membrane from attack by dissolved lithium.

c. New Solid Electrolytes

A large number of ionic solids with conductivities in the aqueous electrolyte range have been developed recently through an extensive research effort at Atomics International.⁽²³⁾ These materials owe their unusual behavior not to impurities, but to intrinsic properties of the crystal structure.⁽²⁴⁾ Unfortunately, the known high-conductivity solids are not compatible with the cathode or anode systems that are under consideration in this program. However, the development of new solid electrolytes with the required chemical properties may be considered.

B. RESULTS OF THE ClF₃ CATHODE STUDY

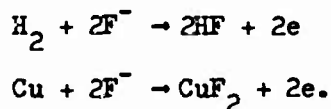
Some equilibrium and steady-state potentials pertinent to this study are considered in Part 1 of this section. Results of the voltammetric measurements are discussed on a broad basis, with reference to these potentials, in Part 2, and a more detailed analysis of the process that appears to be most important on a platinum electrode is given in Part 3.

1. Equilibrium and Steady-State Potentials

Electrode potentials for a number of processes that are of interest in this study are indicated in Figure 6. Values are given on both the hydrogen and the copper-cupric fluoride scales. This approximate chart is intended as a framework to assist in the interpretation of the voltammetric data. Some of the calculated values correspond to solid and gaseous materials, for which free energies are accurately known, rather than to dissolved gases and ions in anhydrous HF, for which detailed thermodynamic data are not available. It may be noted further that the symbol for fluoride ion in HF could be written HF_2^- . At 25°C, the free energy of formation of the bifluoride ion is approximately -12 kcal, based on the process



This contribution tends to cancel, however, in the estimation of potentials for Figure 6, since F^- (or HF_2^-) also appears in the reference electrode reactions:



With a platinum substrate, the potential range in the voltammetric study is limited to an interval of about 2.8 to 3.0 v, which is equal to the decomposition potential for the electrolyte on that metal. On other substrates, the potential limits may be extended somewhat, through the formation of protective films.

Experimentally, the platinum electrodes had an open-circuit potential of +1.47 v vs Cu/CuF_2 following the initial addition of ClF_3 to form a 0.014 M solution. This is consistent with the potential, corresponding to

(Solid lines represent thermodynamic or open-circuit potentials;
broken lines represent potentials under the indicated current drains.)

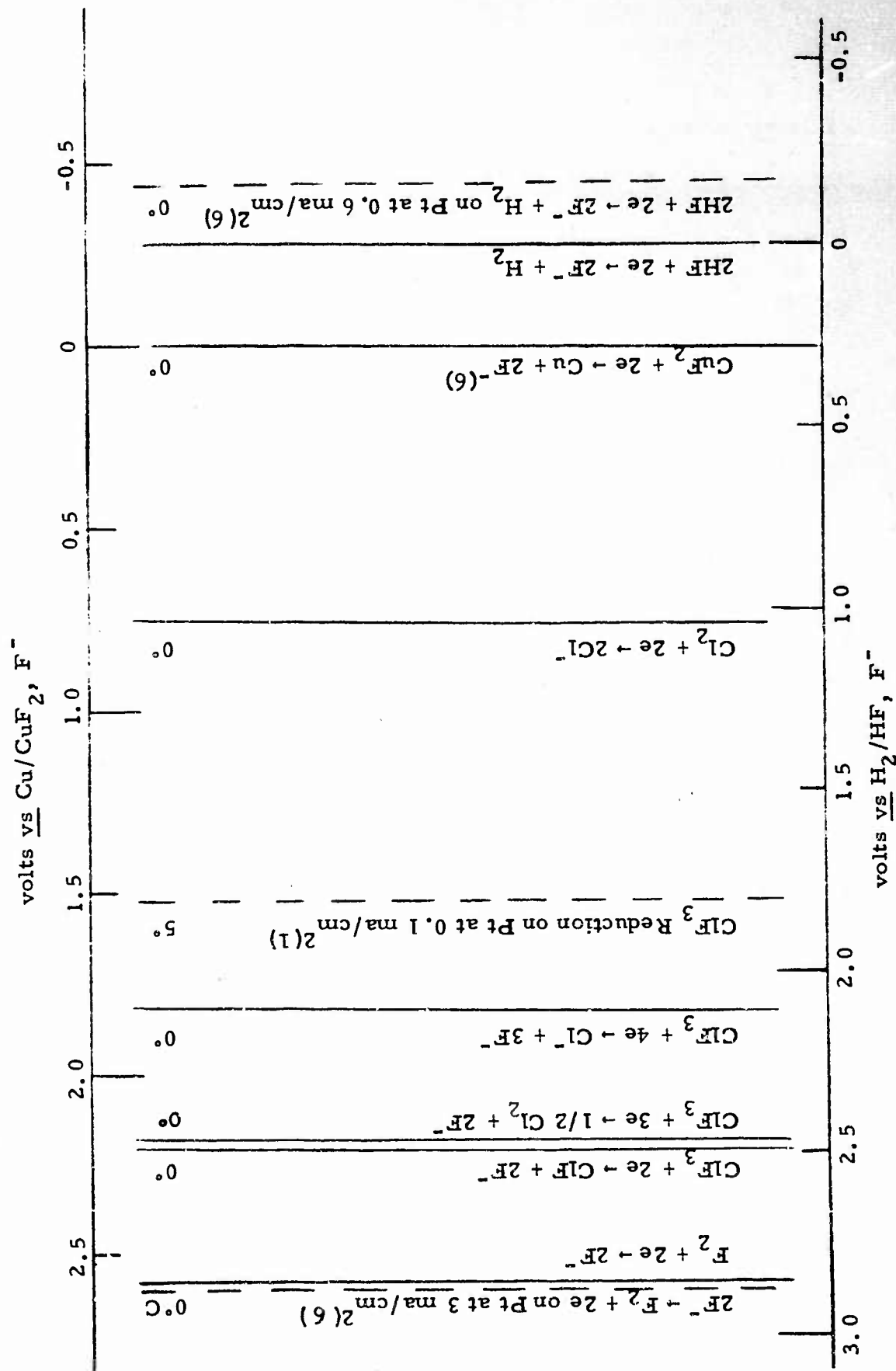


Figure 6. Approximate Electrode Potentials in Hydrogen Fluoride

+1.5 v vs Cu/CuF_2 , which was observed by Smith et al. for 2 M ClF_3 on open circuit in a 0.5 M NaF-HF electrolyte at the same temperature.⁽¹⁾

2. Cyclic Voltammograms

With the cyclic voltammetric technique, a triangular voltage signal is applied to the electrode under investigation, and the resulting current is measured as a function of the applied potential. Linearity of the voltage sweep throughout each half cycle is maintained by potentiostatic control with respect to a reference electrode in which no current flows. In an X-Y recording, the current-potential function forms a closed figure as the system cycles between the selected anodic and cathodic limits. Different processes at the test electrode are displayed as a series of current peaks occurring at characteristic positions on the voltage scale. A reaction that can be reversed electrochemically produces a pair of peaks lying on opposite sides of the zero-current line. This pairing occurs because a reaction product formed, for example, in the cathodic sweep, remains temporarily near the electrode; this material can be reoxidized on the return anodic sweep if there are no complicating factors. The separation between the anodic and cathodic peaks provides an index of the electrochemical reaction rate.⁽²⁶⁾

A cyclic voltammogram for 0.014 M ClF_3 is shown in Figure 7, with potential limits of +2.38 v and -0.28 v vs Cu/CuF_2 . The displaced curve in the lower section is the initial cathodic sweep. After three cycles, the traces became essentially coincident, showing that a steady state had been reached. Three cathodic processes are nicely resolved in this figure. The first peak, at +1.36 v, had a corresponding anodic peak at +1.43 v (Peak 4). This relationship was confirmed in Figure 8, where the scan was restricted

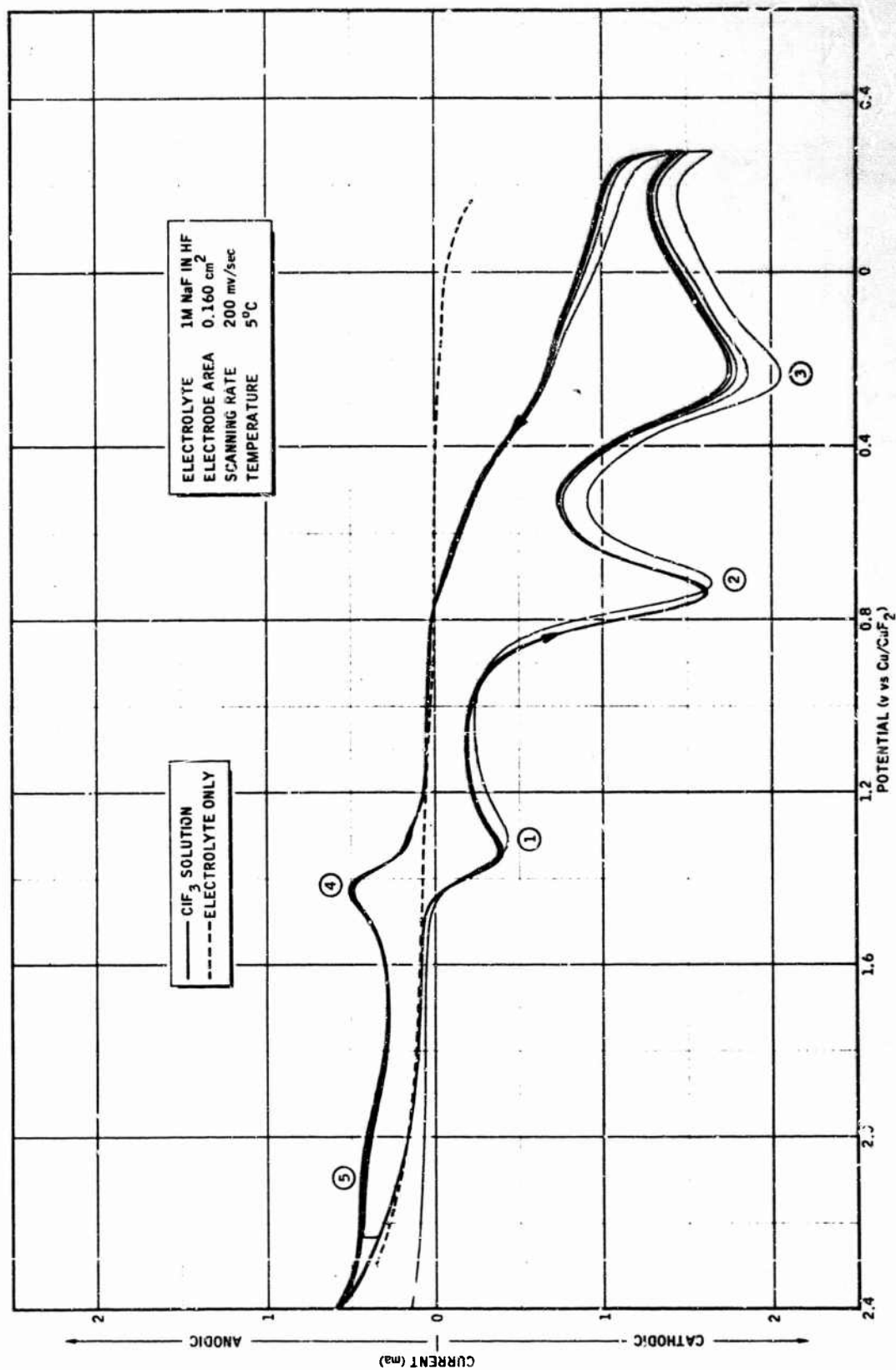


Figure 7. Wide-Span Cyclic Voltammogram for 0.014 M ClF₃ at a Platinum Electrode

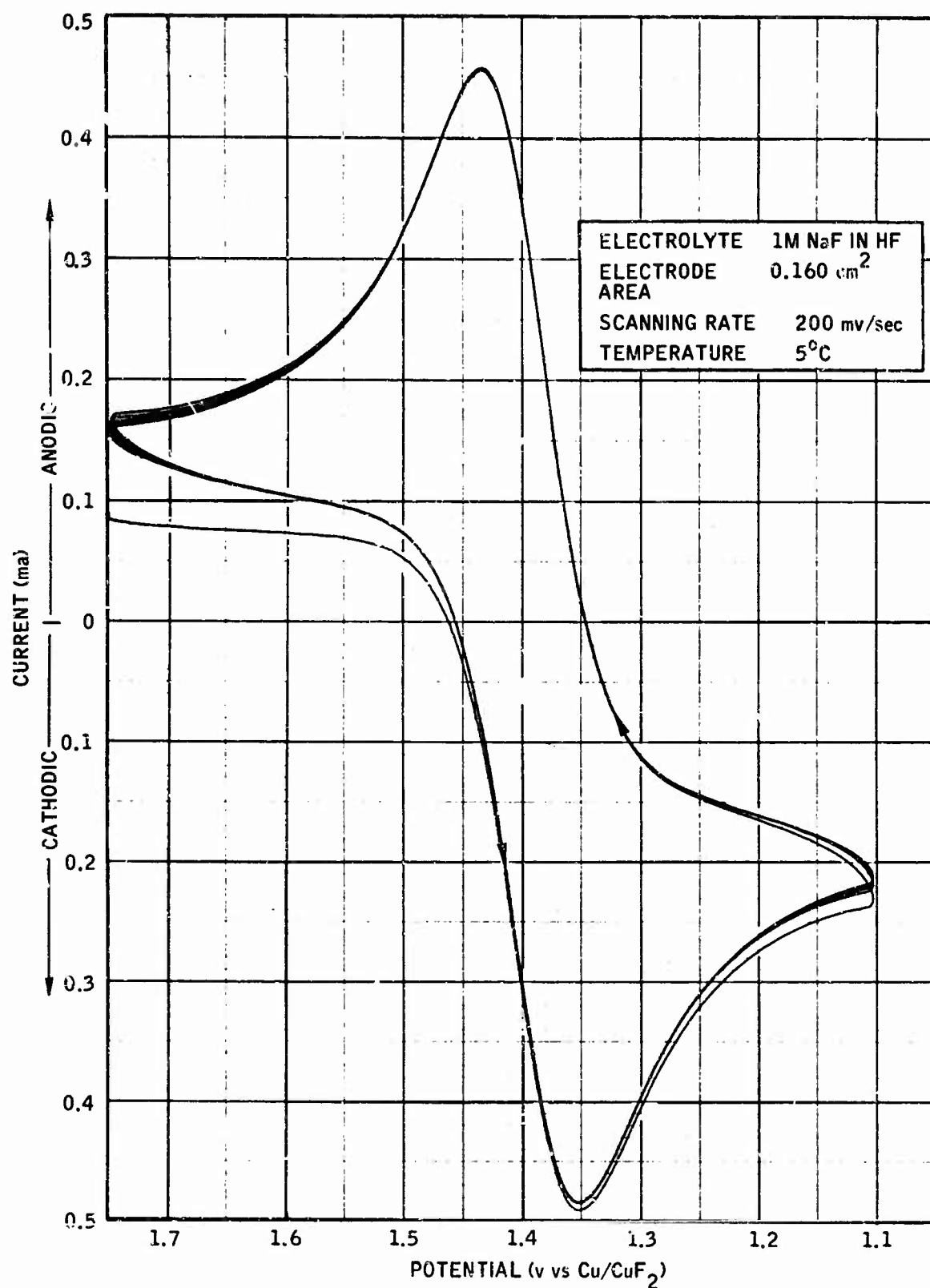
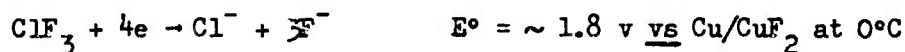


Figure 8. Narrow-Span Cyclic Voltammogram for 0.014 M ClF_3 at a Platinum Electrode

to the potential range covered by these two reactions. The second and third cathodic processes produced well-defined peaks at +0.74 v and +0.34 v, respectively, but gave no direct evidence of reverse reactions. Finally, a broad current increase at position 5 on the anodic sweep indicated another oxidation process within the ClF_3 reaction scheme, possibly one involved in the formation of ClF_5 .⁽²⁷⁾

The three cathodic peaks occurred at potentials considerably more negative than any of the approximate standard potentials for ClF_3 reduction that are given in Figure 6. Peaks 1 and 4 fall about 0.4 v from the calculated potential for the complete reduction of ClF_3



but the actual reaction is probably less complex, since the couple shows a rather high degree of reversibility. This reaction is discussed further in Section III-B-3. Peaks 2 and 3 involve still larger displacements from the estimated region for the thermodynamic reduction processes. The potentials for incipient hydrogen and fluorine evolution, which are evident from current increases near the scan limits (Figure 6), confirm that the Cu/CuF_2 reference electrode was functioning properly.⁽⁶⁾ The second cathodic peak lies near 0.76 v vs Cu/CuF_2 , which is the estimated standard potential for Cl_2/Cl^- at 0°C . It should be noted, however, that Cl^- is unstable in the presence of ClF_3 and may be able to exist only as an intermediate in localized regions of low ClF_3 concentration. This might account for the absence of a Cl^- oxidation peak in the present system. Peaks 2 and 3 in Figure 7 are four to five times higher than Peaks 1 and 4. The different currents may not be simply related in a system of this kind, or

predictable from the ClF_3 reactions listed in Table 1, but the higher peaks are consistent with larger numbers of electrons, n , in the successive cathodic processes. In some of the simpler situations, the peak current is proportional to $n^{3/2}$.⁽²⁸⁾ It is clear from these general observations that additional voltammetric data are needed, particularly on solutions of Cl_2 , Cl^- or HCl , and Cl_2 - ClF_3 mixtures, before more definite interpretations can be made. Solutions of ClF are also desirable, but these are more difficult to prepare.

Effects of stirring and of increased ClF_3 concentration were investigated briefly. Figure 9 shows a wide-span voltammogram which was recorded with the magnetic stirrer in operation. The third cathodic process showed a two-fold increase in current, due to stirring, while the other currents were not greatly affected at the scanning rate of 200 mv/sec. Again, an interpretation at this stage would be speculative. Peak current-concentration ratios for the various electrode processes at nominal ClF_3 concentrations of 0.014 M and 0.028 M are given in Table 6. The currents were somewhat lower in the 0.014 M solution after it stood overnight, possibly due to reaction of ClF_3 with the metal tubing above the cell inlet and outlet. Roughly, doubling the ClF_3 concentration doubled the various currents, with the exception of that for anodic Peak 5. This current was approximately the same in the two solutions. A current independent of bulk concentrations is usually associated with a surface-controlled process such as adsorption or film formation.

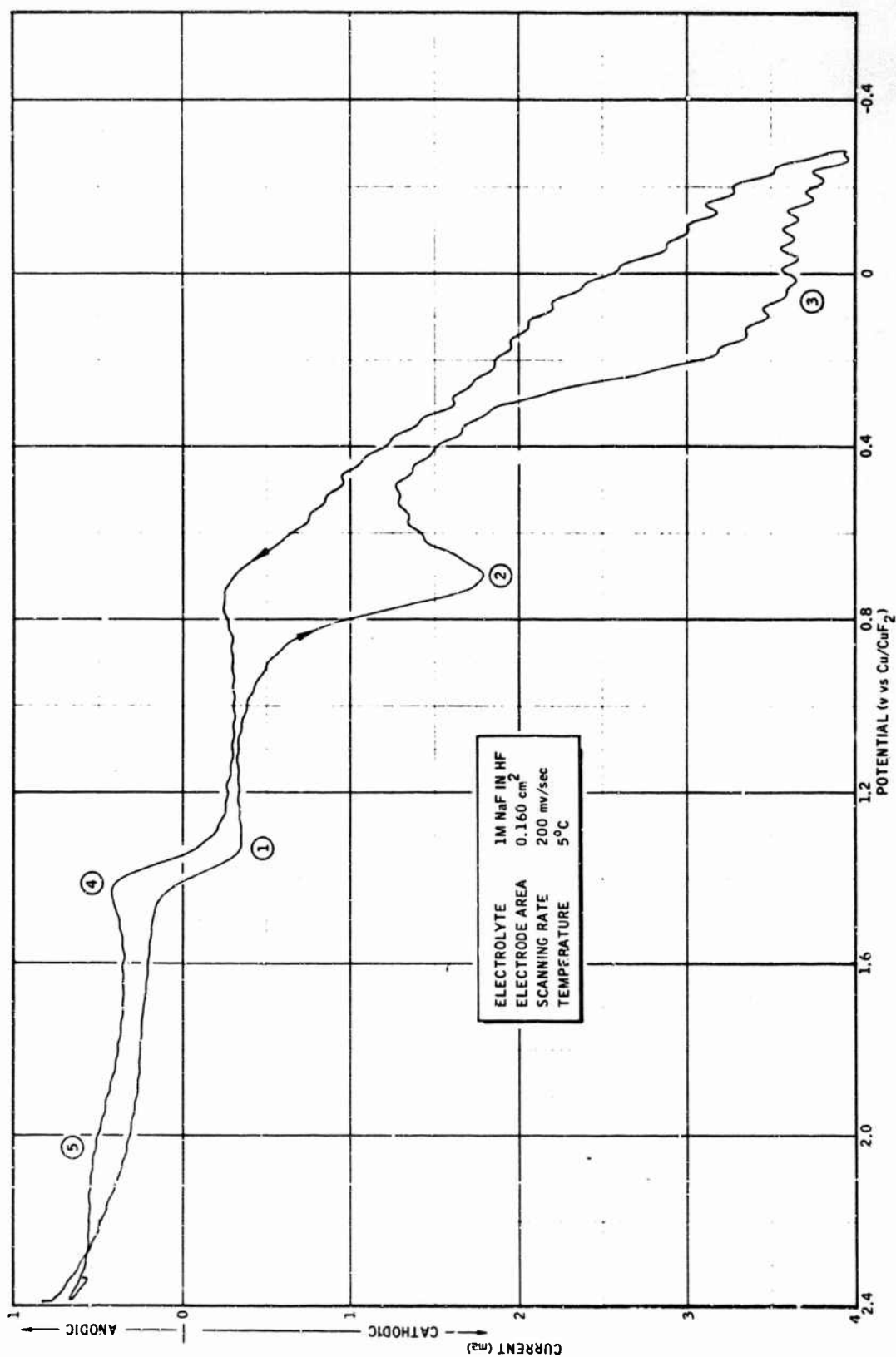


Figure 9. Wide-Span Cyclic Voltammogram for 0.014 M ClF_3 at a Platinum Electrode with Stirring

TABLE 6

PEAK CURRENT-CONCENTRATION RATIOS^a FOR ClF_3 ELECTRODE PROCESSES

ClF ₃ Solution		$\Delta i_p / \Delta C^b$ (ma x μ /mole)		i_p / C (ma x μ /mole)				
Concentration (moles/ μ)	Preparation	Peak 1 ^c Cathodic	Peak 4 ^c Anodic	Peak 1 ^c Cathodic	Peak 4 ^c Anodic	Peak 2 Cathodic	Peak 3 Cathodic	Peak 5 Anodic
0.014	Fresh			35	32	115	125	31
0.014	Stood over- night			25	29			
0.028	0.014 M over- night plus incremental 0.014 M	33	29	29	29	100	107 ^d	18

^aPlatinum electrode, area 0.160 cm²; scanning rate 200 mv/sec^bFor incremental 0.014 M ClF₃^cNarrow-span voltammograms^dDecreased gradually with successive scans

3. The Quasi-Reversible Reaction

a. Characterization of the Peak 1 - Peak 4 Process

Certain characteristics of the electrode process can be derived from a more detailed analysis of a cyclic voltammogram such as that shown in Figure 8.^(26,28-30) It can be determined, for example, whether a reaction is reversible or irreversible, kinetically coupled with a homogeneous chemical process, or complicated by adsorption. Several important criteria are based on responses of the curves to changes in the voltage scanning rate.⁽²⁸⁾ Data taken at scanning rates from 20 to 500 mv/sec are given in Table 7 for Peaks 1 and 4 in the ClF_3 curves. For the discussion that follows, it is convenient to define certain electrochemical terms and symbols:

Reversible Process: An electrode reaction that occurs in either direction at a rate too fast to be measured by the technique employed.

Irreversible Process: An electrode process in which the currents for the forward and reverse reactions are separated by a large overvoltage.

Quasi-Reversible Process: A reaction with kinetics intermediate between the reversible and irreversible cases, generally distinguishable from a reversible process only through a detailed analysis of the data.

Voltammetric Symbols:

i Current, controlled by test electrode

i_p Peak current

TABLE 7

CYCLIC VOLTAMMETRIC DATA FOR THE QUASI-REVERSIBLE ClF_3 REACTION

Scanning Rate ^a (mv/sec)	Platinum Electrode No. 1 ^b					Platinum Electrode No. 2 ^b					
	E_p (v vs Cu/CuF_2)		i_p (ma)		$(i_c/i_a)_p$	E_p (v vs Cu/CuF_2)		ΔE_p (mv)	i_p (ma)		$(i_c/i_a)_p$
	Cathodic	Anodic	Cathodic	Anodic		Cathodic	Anodic				
0.014 M ClF_3											
20						1.36	1.43	75	0.106	0.148	0.72
50						1.36	1.43	72	0.182	0.222	0.82
100						1.36	1.44	83	0.230	0.247	0.93
200	1.35 ^c	1.44 ^c	0.485 ^c	0.456 ^c	1.06 ^c	1.35 ^c	1.44 ^c		0.450 ^c	0.440 ^c	1.02 ^c
	1.35 ^c	1.43 ^c	0.496 ^c	0.457 ^c	1.08 ^c	1.35 ^c	1.43 ^c		0.486 ^c	0.455 ^c	1.07 ^c
						1.36	1.44	81	0.349	0.400	0.87
500						1.35	1.45	91	0.56	0.61	0.92
0.028 M ClF_3											
200	1.38	1.47	0.77	0.77	1.00	1.38	1.46		0.81	0.80	1.01
500	1.37	1.47	1.17	1.17	1.00	1.38	1.46		1.23	1.21	1.02

^aInitial potential 1.75 v vs Cu/CuF_2 ; final potential 1.10 v^bElectrode area 0.160 cm²^cFreshly prepared solution

- E Potential vs reference electrode, controlled instrumentally
- E_p Peak potential
- ΔE_p Separation between anodic and cathodic peaks
- n Number of electrons transferred per molecule of reactant
- k_s Standard heterogeneous rate constant for the electrode reaction*

Some characteristics of the Peak 1 - Peak 4 process may be specified from the criteria given by Nicholson and Shain.⁽²⁸⁾ These features are discussed below.

i_p vs \sqrt{v} . Figure 10 shows that the cathodic and anodic peak currents were essentially proportional to the square root of the scanning rate. This relationship is characteristic of an uncomplicated reversible or irreversible process but will not be observed for other situations. Since the peaks were obviously not widely separated, the process may be classified as reversible, or quasi-reversible. No correction was made for the small background current due to the electrolyte. This may account for failure of the lines to intersect the origin exactly.

i_p (cathodic)/ i_p (anodic). The ratio of cathodic and anodic peak currents is reported in Table 7. The trend toward lower ratios at the lower scanning rates suggests the possibility of a reversible charge-transfer process followed by an irreversible chemical reaction. This point requires further confirmation with respect to stability of the initial cathodic product.

E_p (cathodic) vs v . It is apparent in Table 7, for 0.014 M ClF_3 and Platinum Electrode No. 2, that the cathodic peak potential was

*Related to the exchange current I° through $I^\circ = nFk_s C_O^{1-\alpha} C_R^\alpha$, where C_O and C_R are concentrations of the oxidized and reduced species and α is the transfer coefficient.

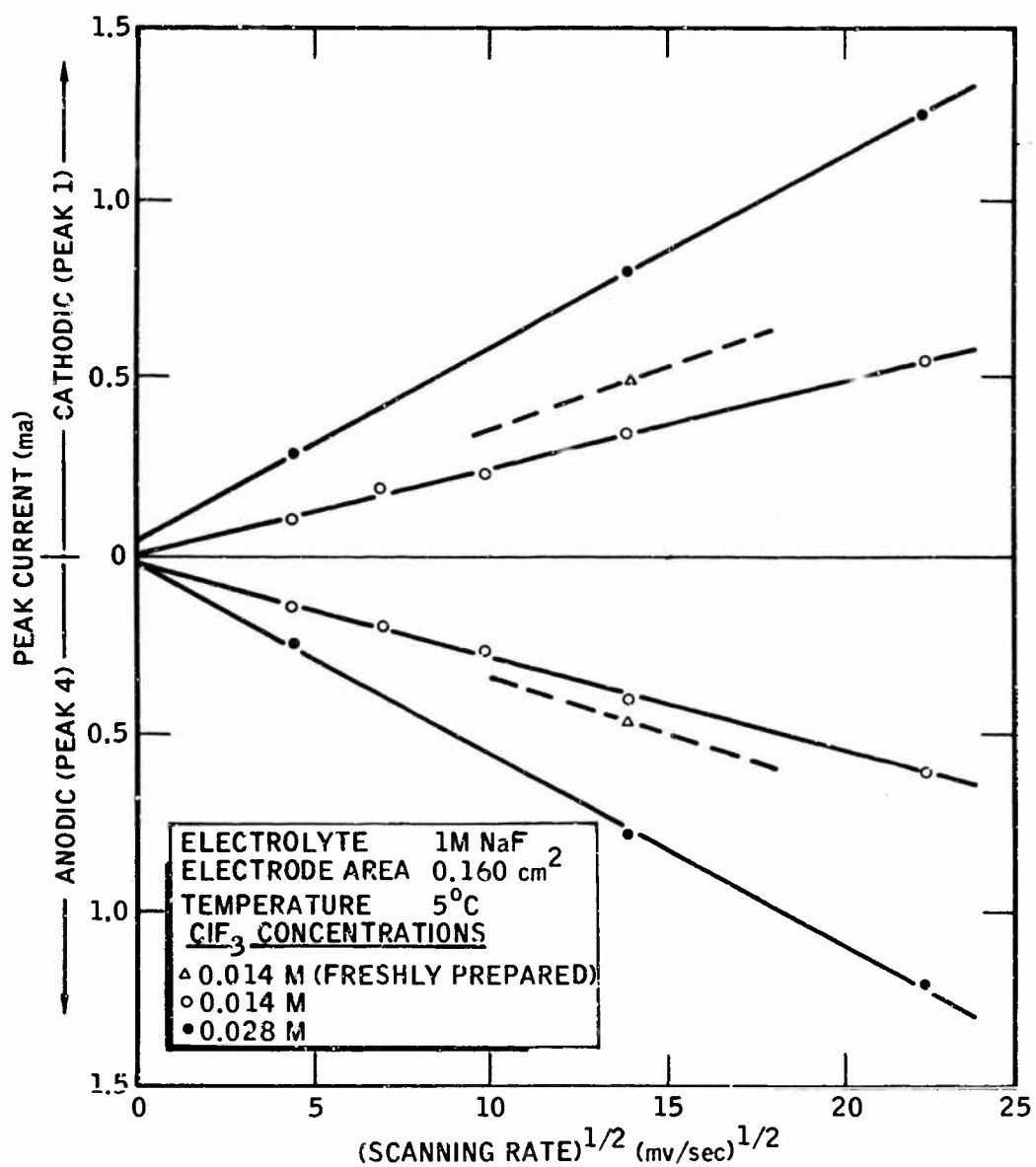


Figure 10. Dependence of Peak Currents on Scanning Rate

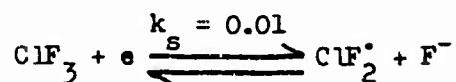
essentially independent of the scanning rate. This too indicates a reversible charge-transfer process.

ΔE_p vs v. The separation of anodic and cathodic peaks varied from 75 mv at 20 mv/sec to 91 mv at 500 mv/sec. This separation could be determined with slightly better precision than the absolute E_p values because ΔE_p was not influenced by alignment of the chart paper with respect to the initial potential. A method for estimating the rate constant from the peak separation was developed by Nicholson, based on the first cycle in a linear-sweep voltammogram.⁽²⁶⁾ Because Reaction 5 interfered at the initial potential for ClF_3 , the steady-state voltammogram obtained on three or more cycles was considered more reliable. The kinetic analysis of ΔE_p data is somewhat approximate for this reason. A unique conclusion is prevented, furthermore, by the fact that n is unknown for the overall reaction. Subject to these restrictions, it was estimated that

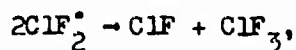
$$k_s = 0.01 \text{ cm/sec if } n = 1$$

$$\text{or } k_s = 0.002 \text{ cm/sec if } n = 2.$$

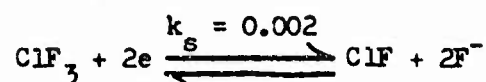
A 1-electron reduction of ClF_3 , yielding a stable product, is difficult to visualize. An unstable product, ClF_2^\bullet , possibly cannot be ruled out at this stage:



The difluoride radical could disproportionate, according to the equation



or participate in other reactions. A 2-electron reduction to ClF seems more likely to produce the well-formed anodic wave that was actually observed:



However, the peak potentials are 0.8 v more negative than those predicted thermodynamically for this couple. Some discrepancies thus remain to be resolved.

Conclusions. In summary of this section, it may be stated that the Peak 1 - Peak 4 process is at least quasi-reversible. Further investigation will be required to determine the nature and stability of the reduction product on platinum as well as other substrates. Comments pertaining to power source applications of ClF_3 are given as Part B-3-b of this section and in the Technological Forecast.

b. ClF_3 as a Secondary Power Source Cathode

The quasi-reversible reaction discussed above must almost certainly be the process involved in the constant-current discharge experiments of Smith et al.⁽¹⁾ Although the cathodic reduction of ClF_3 in HF at substantial current densities was expected from that work, reversibility of the electrode process was not anticipated. This observation presents the possibility of a secondary ClF_3 cathode for high energy electrochemical power sources. For the further development of this concept, it will be necessary to determine the chemical identity of the reduction product and evaluate its recharge capability in measurements extending over longer periods of time.

IV. TECHNOLOGICAL FORECAST

Part A of this section states the problem that was investigated under this contract. Section IV-B indicates the initial, current, and estimated final states of the art. Section IV-C outlines certain technical

implications of the results obtained and suggests approaches for further development work.

A. PROBLEM

The problem investigated under this contract is the evaluation of interhalogen compounds as cathode materials for high energy electrochemical cells operating at ambient or lower temperatures. Chlorine trifluoride was selected for the initial 1-year study.

An efficient cell utilizing an interhalogen cathode and an active light-weight anode such as lithium would be the basic element in a power source providing an exceptionally high energy per unit weight or volume. Theoretically, such a system offers an order of magnitude improvement in energy density over the existing silver-zinc battery. There are indications that it may also be capable of supplying high power densities.

A new power source of this kind would be especially useful in Naval aircraft and missile applications, where weight and volume are at a premium. The extreme reactivity of the chemicals employed would tend to limit the use of the system for general commercial purposes, but it may find special applications where light-weight power sources are required--for example, in the launching and operation of communication and weather satellites. In these areas, an interhalogen cell would compete with the silver-zinc battery, and possibly, with the rechargeable nickel-cadmium cell.

B. STATE OF THE ART, SOLUTION, AND FORECAST

It was known from prior investigations that chlorine trifluoride is an active cathode material when dissolved in anhydrous hydrogen fluoride.⁽¹⁾ The efficiency of this cathode system, i.e., how far the electrode reaction

proceeds to completion, was not known, however, nor was there any information on the parameters governing the reaction rate or the recharge capability. As a result of this program, the electrochemical behavior of chlorine trifluoride has become more clearly defined. Five different electrode reactions have been characterized; two of these constitute a reversible, or near-reversible system. In a lithium-chlorine trifluoride battery, this reversible process could supply as much as 4.8 v per cell. This figure is to be compared with a typical operating voltage of 1.2 v for a single silver-zinc cell. Then, with the assumptions of an unpolarized lithium anode and a 2-electron reduction of chlorine trifluoride (see Section III-B-5), the energy density could be 1100 whr/lb, based on active electrode materials only. A practical figure of 300 to 500 whr/lb might then be realized if the entire cell weight were included. A comparable value for the silver-zinc cell is 90 whr/lb.

In practice, the actual energy density depends on the discharge rate. The electrodes used in these initial experiments on chlorine trifluoride were not porous battery plates, but smooth platinum wires. A current density of 1 ma/cm^2 was easily attained in a solution containing only 0.13 wt % of the active material (0.014 M ClF_3). On this basis, it is estimated that a 20% solution could support a current density of 150 ma/cm^2 on a smooth electrode, with very little power loss due to activation overvoltage. With a porous electrode of proper design, the effective current density would be higher, in proportion to the higher surface area. These estimates predict an efficient, high power-density cathode.

It should be emphasized that this forecast is based on cathode performance only. Problems arising in the lithium anode and the separator, which are discussed in Section III-A, were not taken into account in arriving at the figures given above. Suggested approaches to the solution of these problems are indicated in Section IV-C.

C. SUGGESTIONS AND IMPLICATIONS

The following suggestions are offered for further development of an interhalogen cathode:

- 1) Further evaluation of cathode efficiency by positive identification of the electrochemical reaction products
- 2) Investigation of inexpensive cathode substrates, such as carbon and Monel, to be substituted for platinum, which was used in this study
- 3) Optimization of cathode performance with respect to (a) concentration of the active material, (b) concentration of the sodium fluoride electrolyte, and (c) pretreatment of the cathode substrate
- 4) Determination of temperature effects on cathode performance
- 5) Evaluation of chlorine trifluoride as a cathode material for a secondary battery.

In addition, the continuation of anode and separator development* is recommended:

- 1) Further evaluation of the lithium ammoniate anode⁽³⁾
- 2) Development and investigation of new solid electrolytes as separators for dual-solvent cells

*Discussed in Sections III-A-2 and III-A-3.

- 3) Investigation of lithium-magnesium and lithium-aluminum alloys as anodes for single-solvent cells containing anhydrous hydrogen fluoride.

V. ACKNOWLEDGMENT

Mr. W. F. Goeppinger provided experimental assistance on this program and developed most of the detailed equipment designs.

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13. ABSTRACT <p>Halogen fluoride cathodes offer the prospect of extremely high energy densities when combined with active metal anodes in electrochemical power sources. Chlorine trifluoride, with a theoretical 2120 whr/lb in combination with lithium, is also known to support substantial current densities when dissolved in anhydrous hydrogen fluoride containing an alkali metal fluoride electrolyte. The objective of this program was the further evaluation of chlorine trifluoride as a power source cathode material. A half-cell study was made on dilute ClF_3 solutions at 5°C in 1 M NaF-HF by the cyclic voltammetric technique, using platinum electrodes. Three cathodic and two anodic reactions were observed in wide-span voltammograms on this system. One of the electrode processes showed a high degree of reversibility, which suggests its use in a secondary, as well as a primary, cell. The potential of this couple corresponds to 4.8 v with respect to a lithium anode. Reverse reactions did not occur with the other processes. Further investigation will be required to identify the products the various electrode reactions, and thus to establish, with certainty, the energy densities that might be expected in optimized chlorine trifluoride cells.</p> <p>Pure lithium is chemically incompatible with hydrogen fluoride. A dual-solvent cell containing a liquid lithium anode dissolved in liquid ammonia and an interhalogen cathode in hydrogen fluoride is under consideration by the Navy. Some technical problems involved in the construction of such a cell are discussed in this report, and the possibility of using a solid electrolyte separator is</p> <p>(Contd on p. 45)</p>		

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ABSTRACT (Contd)

suggested. Lithium alloy anodes that would function directly in HF are also considered for an alternative single-solvent cell.

Recommendations for further work on the ClF_3 cathode include the identification of electrode reactions, optimization studies using less expensive substrates than platinum, and the investigation of temperature dependence.